



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 947 874 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
06.10.1999 Bulletin 1999/40

(51) Int Cl.6: G02F 1/161, G02F 1/15

(21) Application number: 99850052.4

(22) Date of filing: 30.03.1999

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 30.03.1998 JP 10340698

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(54) Method for producing an electrochromic device

(57) Disclosed is a method for producing an electrochromic device providing an opening in the surface of each of the two electrically conductive substrates of the cell, not in the end surface of the opposed substrates, to fill the inside of the hollow cell with an electrolyte or

the precursor thereof by injecting through the injection port, to seal temporarily the injection port with a material which can be deformably inserted into the port and to seal secondarily the temporarily sealed port by applying thereon only an adhesive or a sheet-like member over the adhesive.

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Description

[0001] This invention relates to a method for producing an electrochromic device.

[0002] An electrochromic device is generally produced by sealing the periphery, except for a portion thereof, of a pair of electrically conductive substrates, at least one of which is transparent, placed in a spaced-apart opposing relationship so as to assemble a cell having an injection port formed by the unsealed portion and filling the inner space of the cell by charging through the port an electrolyte or the precursor thereof in a vacuum. The injection port of the cell is then sealed by filling and curing therein a photo-setting or thermosetting acrylic resin or epoxy resin adhesive.

[0003] However, such a method for sealing or closing the port requires a step of removing the electrolyte adhered around the injection port prior to filling the adhesive. If the electrolyte is not removed completely, the adhesive can not seal the port sufficiently. Furthermore, the above sealing method fails to obtain satisfactory sealing strength due to an insufficient cure of the adhesive caused by the contact thereof with the electrolyte.

[0004] Japanese Laid-Open Patent Publication Nos. 2-114237 and 6-250230 disclose a two-step sealing method to solve the foregoing problems.

[0005] Japanese Laid-Open Patent Publication No. 2-114237 discloses a method which comprises a primary sealing and a secondary sealing. In this method, first of all, there is prepared a cell having an opening formed in a selected portion of the peripheral edges of a pair of substrates in opposing relation. After an electrolyte is charged through the opening, the primary sealing is conducted by coating an epoxy resin adhesive to the opening while an external pressure is vertically applied to the substrates followed by releasing the pressure to allow the sealant to enter into the inside of the opening and cure therein. After a certain period of time, the secondary sealing is carried out by coating an epoxy resin adhesive on the peripheral edges of the substrate including the primary sealed portion and allowing the adhesive to cure it self.

[0006] This method is recognized as being applicable to the production for a electrochromic device of a relatively small size. However, the method is not always suitable for the production for an electrochromic device of a relatively large size because the primary sealing requires the process of applying an external pressure onto the cell. Furthermore, this two-step sealing method is mainly focused on the injection port (opening) provided on the end surface of the cell. Therefore, when this method is employed for producing the large electrochromic device, there may arise a risk that the adhesive would peel off due to the stress applied to the sealing portion upon transportation of the device even though the sealing is completed in a satisfactory manner.

[0007] Japanese Laid-Open Publication No. 6-250230 proposes a method by which an electrolyte injection port is sealed with a radiation cure type adhesive and then sealed with an epoxy resin adhesive so as to be overlapped with the former adhesive. However, with this method the above risk can not be removed because it also attempts to solve the above problem by providing the electrolyte injection port in the end surface of the cell.

[0008] An object of the invention is to provide a method for producing an electrochromic device of which sealing portion of the electrolyte injection port is free from the peel off of the adhesive by providing the electrolyte injection port in one of the two opposing substrates, not in the peripheral edge of the cell, even upon the production of a large size electrochromic device on which stress would possibly applied during the transportation of the device.

[0009] Another object of the invention is to provide a method for producing an electrochromic device. The method can avoid completely the contact between an electrolyte and an adhesive to be used for sealing the electrolyte injection port and thus is also free from a risk that the curing reaction of the adhesive is hindered.

[0010] According to the invention, there is provided a method for producing an electrochromic device which comprises:

- (a) a step of assembling a hollow cell constituting an electrochromic device by opposing two electrically conductive substrates, at least one of which is transparent and either of which is provided with an injection port for an electrolyte, in a spaced-apart relationship with each other and sealing together the entire peripheral edges of the opposed substrates;
- (b) a step of filling the inside of the hollow cell with an electrolyte or the precursor thereof by injecting through the injection port;
- (c) a step of sealing temporarily the injection port with a material which can be deformably inserted into the injection port; and
- (d) a step of sealing secondarily the temporarily sealed port by applying thereon only an adhesive or a platelike member over the adhesive.

[0011] An electrically conductive substrate used for the inventive method means literally a substrate functioning as an electrode. The electrically conductive substrate may be that of which substrate itself is electrically conductive or that of which is not electrically conductive but has an electrode layer disposed on the surface contacting the layer of an electrolyte.

[0012] Such an electrically conductive substrate may be iron, copper, silver, aluminum, tin, lead, gold and zinc and alloys thereof. The non-electrically conductive substrate may be any type of substrate as long as it has a smooth surface. Specific examples are substrates made of a material such as plastics (synthetic resin), glass, wood and stone.

[0013] The electrochromic device produced by the invention includes a pair of such electrically conductive substrates 5 one of which is necessarily transparent. Such an electrically conductive transparent substrate may be produced by laminating an electrode layer on a transparent substrate. The transparent substrate may be colored or colorless glass as well as colored or colorless plastic (synthetic resin). Eligible plastics for this purpose are polyethylene terephthalate, polyamide, polysulfone, polyether sulfone, polyether etherketone, polyphenylene sulfide, polycarbonate, polyimide, polymethyl methacrylate and polystyrene.

[0014] The term "transparent" used herein designates optical transmission ranging from 10 to 100 %. The substrate 10 used for the invention may be flat or curved and may be deformable by stress as long as it has a smooth surface at room temperature.

[0015] It is preferred that the electrode layer to be laminated on the non-electrically conductive substrate is transparent. It is requisite that at least the electrode layer to be laminated on the transparent substrate is transparent. Eligible 15 for the electrode layer are a thin film of metal such as gold, silver, chrome, copper and tungsten or a metal oxide such as ITO ($In_2O_3\cdot SnO_2$), tin oxide, silver oxide, zinc oxide and vanadium oxide.

[0016] The thickness of the electrode is selective within the range of usually 10 to 1,000, preferably 50 to 300 nm. The surface resistance of the electrode may be selected suitably but usually in the range of 0.5 - 500, preferably 1 - 50 Ω/sq .

[0017] No particular limitation is imposed on the formation method of the electrode layer. Any suitable conventional 20 methods may be selected depending upon the metal and metal oxide constituting the electrode. In general, the formation of the electrode layer is carried out by vacuum evaporation, ion plating, sputtering and a sol-gel method. In any case, the formation of the electrode should be conducted while maintaining the temperature of the substrate within the range of 100-350 °C.

[0018] The electrode layer may partially provided with an opaque electrode-activator in order for the purpose of 25 imparting oxidation-reduction capability and increasing electric double layer capacitance. In this case, if it is necessary to maintain the transparency of the electrode, the optical transmission of the whole electrode is kept within the range of 10-100 %.

[0019] Electrode activators eligible for the purpose of the invention include a metal such as copper, silver, gold, 30 platinum, iron, tungsten, titanium and lithium, an organic material having oxidation-reduction capability such as polyaniline, polythiophene, polypyrrole and phthalocyanine, a carbon material such as active carbon and graphite and a metal oxide such as V_2O_5 , W_0_3 , MnO_2 , NiO and Ir_2O_3 and mixtures thereof. These electrode activators may be integrated to the electrode with a binder resin.

[0020] The opaque electrode activator may be applied onto an electrode by forming over an ITO transparent electrode 35 a composition comprising an active carbon fiber, graphite and an acrylic resin in the shape of stripes or by forming on a thin-film of gold (Au) a composition comprising V_2O_5 , acetylene black and butyl rubber in a meshed pattern.

[0021] One of the two electrically conductive substrates used for the inventive has in the surface an opening of 0.5-10, preferably 2-6 mm Ø which opening is used as an injection port for an electrolyte.

[0022] The cell for the electrochromic device according to the invention is produced by opposing the two electrically 40 conductive substrates, one of which is transparent, in a spaced-apart relation and sealing the whole peripheral edges of the opposed substrates. If the electrically conductive substrate is one obtained by laminating an electrode layer thereon, the electrode layer is placed to face the inside of the cell. The space between the opposed substrates is within the range of usually 30-1,000, preferably 200 - 500 μm .

[0023] Needless to mention, an electrochromic device contains an electrochromic material. Such an electrochromic 45 material may be mixed in an electrolyte layer or formed into the electrochromic layer separately from the electrolyte layer. The electrochromic layer may be arranged anywhere the inside of the cell. In general, prior to the assembly of the cell, the electrochromic layer may be arranged on at least one or both of the electrode layers on the electrically conductive substrates. When the electrochromic material is mixed into the electrolyte layer, there may be employed a method in which to inject the mixture of an electrolyte or the precursor thereof and the electrochromic material into the 50 cell.

[0024] The electrochromic material may be exemplified by substances colored, bleached or discolored by electrochemical oxidation or reduction such as Mo_2O_3 , Ir_2O_3 , NiO , V_2O_5 , W_0_3 , biogen, polythiophene, polyaniline, polypyrrole, metal phthalocyanine and ferrocene.

[0025] The electrochromic layer may be formed solely from the electrochromic material or may be formed from the 55 electrochromic material and the matrix component thereof, the former being preferred. The electrochromic layer has a thickness in the range of usually 10nm-1 μm , preferably 50-800nm.

[0026] There may be employed any conventional method for forming the electrochromic layer such as vacuum evaporation, ion-plating, sputtering, electrolytic polymerization, dip coating and spin coating.

[0027] No particular limitation imposed on a sealant used for sealing the peripheral edges of the opposed electrically conductive substrates as long as it can seal up the device so as to isolate the interior thereof from its surroundings and so as to prevent a component such as moisture, oxygen and carbon monoxide adversely effecting the performances of the device from permeating into the interior of the device. Therefore, eligible sealants are exemplified by synthetic resins including polyester such as polyethylene terephthalate, polyamide, polysulfone, polyether sulfone, polyether ether-ketone, polyphenylene sulfide, polycarbonate, polyimide, polymethyl methacrylate, polystyrene, tricellulose acetate, polymethylpentene, polysiloxane, polyethylene, polypropylene, polycellulose acetate, phenolic resin, urea resin, epoxy resin, polyvinyl acetate, polyvinyl acetal, polyvinyl alcohol, acrylic and methacrylic esters and, cyanoacrylate; natural rubbers; and synthetic rubbers such as isoprene rubber, butadiene rubber, styrene-butadiene rubber, butyl rubber, ethylene-propylene rubber, chloroprene rubber, chlorosulfonated polyethylene, nitrile rubber, urethane rubber, polysulfide rubber, acrylic rubber, epichlorohydrin rubber, silicone rubber, fluorine rubber and hydrogenated nitrile rubber.

[0028] Alternatively, hardening resins are also eligible for the sealant. There is no particular limitation to the hardening resins and thus various hardening type of resins are eligible such as those cured by heat and electromagnetic ray.

[0029] Eligible hardening resins are phenolic resin, urea resin, epoxy resin, polyvinyl acetate, polyvinyl acetal, polyvinyl alcohol, acrylic and methacrylic esters, cyanoacrylate and polyamide. These may be used singular or in combination. Further alternatively, these resins may be modified by adding fillers. Among these, particularly preferred are an epoxy resin and an acrylic-modified epoxy resin. Preferred acrylic-modified epoxy resins are those containing 0.01-0.3 mol of acrylic residue per mol of epoxy residue, preferably 0.05-0.2 mol of acrylic residue per mol of epoxy residue.

[0030] When the peripheral edges of the opposed electrically conductive substrates are sealed, it is preferred to use a spacer for adjusting the width of the space between the substrates. The spacer needs to be non-electrically conductive but may have sheet-, sphere-, fiber- or bar- like shape.

[0031] There may be employed any suitable method for sealing the electrically conductive substrates such as the following methods:

- 25 (1) Inserting the sealing material having been processed and formed in conformity with the shape of the electrically conductive substrates therebetween;
- (2) Coating the above-mentioned hardening resin paste in a desired shape over the surface of the substrate using a known printing method;
- 30 (3) Coating the sealant over the surface of the substrate; and
- (4) Forming the sealant discharged from a nozzle into a suitable pattern on the substrate by moving the nozzle.

[0032] Among these, particularly preferred is method (4).

[0033] The sealant may be applied to either one or both of the substrates.

[0034] When the hardening resin is applied to the substrate, it is hardened after the substrates are laminated. Needless to mention, the hardening is effected depending on the resin used.

[0035] If a thermal-hardening resin is used, there may be used such a resin hardening at room temperature. If a thermal-hardening resin requiring heat to be hardened is used, it is selected from the resins which harden at a temperature ranging from room temperature to 150 °C, preferably from room temperature to 100 °C. The period of time required for hardening is selected to an extent that electrochromic characteristics are not adversely effected, preferably from the range within 24 hours, more preferably from the range within one hour.

[0036] According to the invention, an electrolyte or the precursor thereof is injected into the cell through the openings provided in one of the electrically conductive substrates forming the cell. Hereinafter, the descriptions are made with respect to the electrolyte and the precursor thereof.

[0037] Although the electrolyte used for the electrochromic device produced by the inventive method may be any type of electrolytes as long as they can color and bleach the electrochromic material contained in the device, preferred are those having an ion conductivity of more than 1×10^{-7} S/cm at room temperature. The electrolyte may be of liquid, gel or solid. Solid electrolytes are particularly preferred for the purpose of the invention.

[0038] Eligible liquid electrolytes are those dissolving a supporting electrolyte such as salts, acids and alkalis in a solvent. Any suitable solvents may be used as long as they can dissolve the supporting electrolyte. Particularly preferred are those having polarity. Specific examples of such a solvent include water and organic polar solvents such as meth-

anol, ethanol, propylene carbonate, ethylene carbonate, dimethylsulfoxide, dimethoxyethane, acetonitrile, *t*-butyrolactone, *t*-valerolactone, sulforan, 1,3-dioxane, N,N-dimethylformamide 1,2-dimethoxyethane and tetrahydrofuran. Preferred are propylene carbonate, ethylene carbonate, dimethylsulfoxide, dimethoxyethane, acetonitrile, *t*-butyrolactone, sulforan, 1,3-dioxane, N,N-dimethylformamide, 1,2-dimethoxyethane and tetrahydrofuran. These may be used singular or in combination.

5 [0039] Although not restricted, salts used as the supporting electrolyte may be alkali metal salts, inorganic ion salts such as alkali earth metal salts, quaternary ammonium salts and cyclic quaternary ammonium salts. Specific examples of such salts include alkali metal salts of lithium, sodium or potassium such as LiClO₄, LiSCN, LiBF₄, LiAsF₆, LiCF₃SO₃, LiPF₆, LiI, NaI, NaSCN, NaClO₄, NaBF₄, NaAsF₆, KSCN and KCl, quaternary ammonium salts or cyclic quaternary ammonium salts such as (CH₃)₄NBF₄, (C₂H₅)₄NBF₄, (n-C₄H₉)₄NBF₄, (C₂H₅)₄NBR, (C₂H₆)₄NClO₄, and (n-C₄H₉)₄NClO₄ and mixtures thereof.

10 [0040] Acids used as the supporting electrolyte may be exemplified by inorganic acids and organic acids which include sulfuric acid, hydrochloric acid, phosphoric acid, sulfonic acid carboxylic acid.

15 [0041] Alkalies used as the supporting electrolyte include sodium hydroxide, potassium hydroxide and lithium hydroxide.

[0042] The gelatinized-liquid electrolyte may be those which are gelatinized or made to be viscous by adding a polymer or a gelatinizer to the above-mentioned liquid electrolytes.

20 [0043] Preferred examples of such a polymer are polyacrylonitrile, carboxymethylcellulose, polyvinyl chloride, polyethylene oxide, polyurethane, polyacrylate, polyamide, polyacrylamide, cellulose, polyester, polypropyleneoxide and nafion.

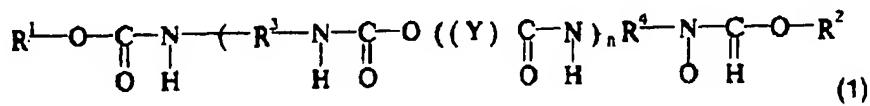
25 [0044] Preferred examples of the gelatinizer are oxyethylenemethacrylate, oxyethyleneacrylate, urethaneacrylate, acrylamide and agar-agar.

[0045] The gelatinized-liquid electrolyte is sandwiched between the opposed electrically conductive substrates by injecting into the cell the mixture of the precursor monomer of a polymer or the precursor of the gelatinizer and a liquid electrolyte and then polymerizing or gelatinizing the mixture.

30 [0046] There is no particular limitation to the solid electrolyte if it is solid at room temperature and ion conductive. Preferred examples of such solid electrolyte are polyethyleneoxide, the polymer of oxyethylenemethacrylate, nafion, polystyrene sulfonate, Li₃N, Na- β -Al₂O₃ and In(HPO₄)₂H₂O. Particularly preferred are polymeric solid electrolytes derived from polymerization of a polyethyleneoxide-based compound, an oxyalkyleneacrylate-based compound or a urethaneacrylate-based compound used as the main component of the precursor.

35 [0047] A first example of such a polymeric solid electrolyte is one obtained by solidifying a composition (hereinafter referred to as Composition A) which is used as a precursor and comprises an organic polar solvent, a supporting electrolyte and a urethaneacrylate represented by the formula

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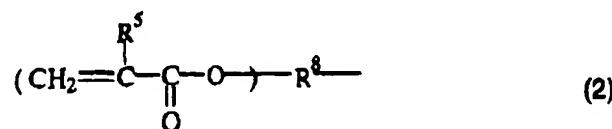


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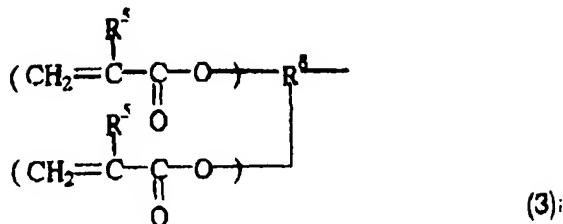
wherein R¹ and R² may be the same or different and are each a group of formula (2), (3) or (4), R³ and R⁴ may be the same or different and are each a C₁-C₂₀, preferably C₂-C₁₂ divalent hydrocarbon residue, Y is selected from a polyether unit, a polyester unit, a polycarbonate unit and the mixed unit thereof and n is an integer of 1-100.

45 [0048] Formulae (2), (3) and (4) are represented by

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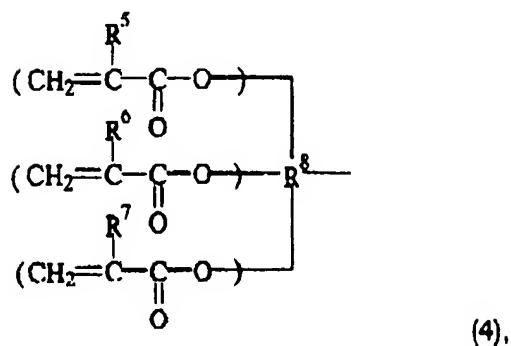


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and



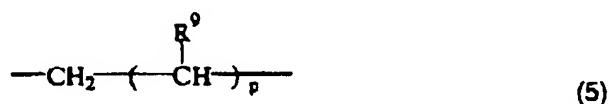
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respectively

30 wherein R^5 , R^6 and R^7 may be the same or different and are each a hydrogen atom or a $\text{C}_1\text{-}\text{C}_3$ alkyl group and R^8 is a $\text{C}_1\text{-}\text{C}_{20}$, preferably $\text{C}_2\text{-}\text{C}_8$ organic residue of divalent through quatervalent. Such organic residues may be a hydrocarbon residue such as alkyltolyl, alkyltetratolyl and alkylene of the formula

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wherein R^9 is a $\text{C}_1\text{-}\text{C}_3$ alkyl group or hydrogen, p is an integer of 0-6 and if p is greater than 2 the groups of R^9 may be the same or different.

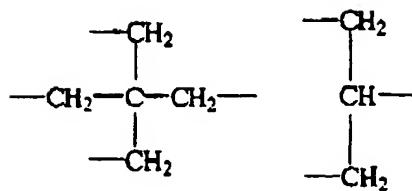
[0049] The hydrocarbon residue may be a group part of which hydrogen atoms are substituted by an oxygen-containing hydrocarbon group such as a $\text{C}_1\text{-}\text{C}_6$, preferably $\text{C}_1\text{-}\text{C}_3$ alkoxy group and a $\text{C}_6\text{-}\text{C}_{12}$ aryloxy group. Specific examples of group R^8 in formulae (2) thorough (4) are those represented by the following formulae:

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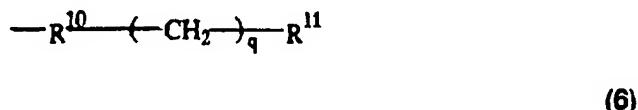
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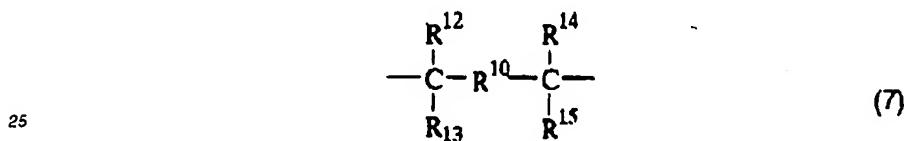
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[0050] Each of the divalent hydrocarbon residues represented by R^3 and R^4 in formula (1) is exemplified by a divalent chain-like hydrocarbon group, an aromatic hydrocarbon group and an alicyclic-containing hydrocarbon group. Specific examples of the chain-like divalent hydrocarbon group are those represented by formulae (6) through (8)

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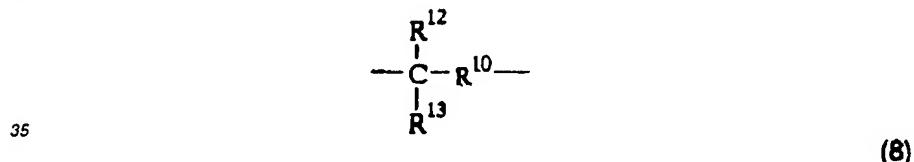


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and

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wherein R^{10} and R^{11} may be the same or different and are each a phenylene group, a phenylene group having an alkyl substituent, a cycloalkylene group and a cycloalkylene group having an alkyl substituent, R^{12} , R^{13} , R^{14} and R^{15} may be the same or different and are each a hydrogen atom or a C_1 - C_3 alkyl group and q is an integer of between 1 and 5.

[0051] Specific examples of the groups R^3 and R^4 in formula (1) are those represented by the following formulae

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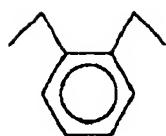


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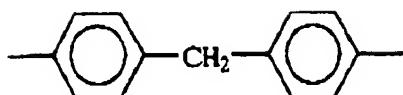
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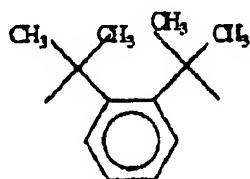
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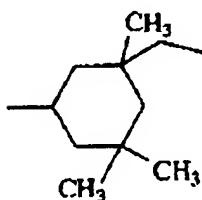
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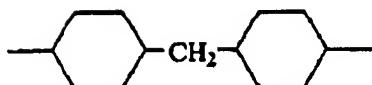
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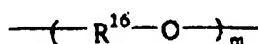
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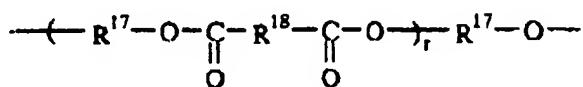
[0052] In formula (1), Y indicates a polyether unit, a polyester unit, a polycarbonate unit and mixed unit thereof. Each of these units is represented by the following formulae :

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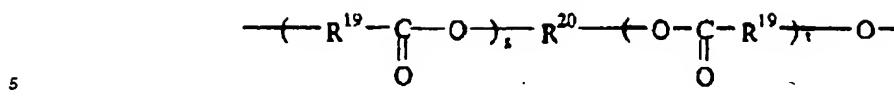
(a)

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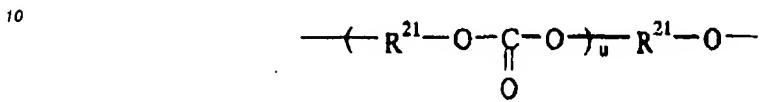


(b)

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and



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wherein R^{16} through R^{21} may be the same or different and are each a $\text{C}_1\text{-C}_{20}$, preferably $\text{C}_2\text{-C}_{12}$ divalent hydrocarbon residue, $\text{C}_1\text{-C}_6$ being particularly preferred for R^{19} , m is an integer of 2-300, preferably 10-200, r is an integer of 1-300, preferably 2-200, s is an integer of 1-200, preferably 2-100, t is an integer of 1-200, preferably 2-100 and u is an integer of 1-300, preferably 10-200.

20 [0053] R^{16} through R^{21} are preferably straight or branched alkylene groups among which methylene, ethylene, trimethylene, tetramethylene, pentamethylene, hexamethylene and propylene groups are preferred for R^{16} and ethylene and propylene groups are preferred for R^{16} , R^{17} and R^{19} through R^{21} .

25 [0054] Each unit represented by formulae (a) through (d) may be a copolymer of the same or different units. In other words, if there exist a plurality of the groups of each R^{16} through R^{21} , the groups of each R^{16} , R^{17} , R^{18} , R^{19} , R^{20} and R^{21} may be the same or different. Preferred examples of such copolymers include a copolymer of ethylene oxide and a copolymer of propylene oxide.

30 [0055] In formula (1), n is preferably an integer of 1-50, more preferably 1-20. The urethaneacrylate of formula (1) has a molecular weight in the range of 2,500 - 30,000, preferably 3,000 - 20,000.

35 [0056] The urethaneacrylate has preferably 2-6, more preferably 2-4 functional groups per molecule.

40 [0057] The urethaneacrylate may be prepared by any suitable conventional methods.

45 [0058] There is no limitation to the organic polar solvent contained in Composition (A) as long as it has a polarity and can dissolve the electrolyte. Preferred are propylene carbonate, ethylene carbonate, butylene carbonate, γ -butyrolactone, sulfolane, 1,3-dioxane, N,N-dimethylformamide, 1,2-dimethoxyethane, acetonitrile and tetrahydrofuran. These solvents may be used singular or in combination. The organic polar solvent is added in an amount of 100 - 1,200, preferably 200 - 900 weight-parts per 100 parts of the urethaneacrylate. Too less amount of adding the organic polar solvent results in insufficient ion conductivity, while too much amount causes a reduction in mechanical strength.

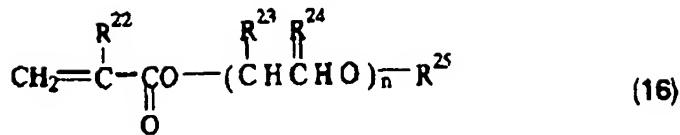
50 [0059] The supporting electrolyte contained in Composition (A) is selected depending on the usage of the device. Generally, the above-described liquid electrolytes are preferably used. The supporting electrolyte should be added in an amount of 0.1-30, preferably 1-20 weight percent of the organic polar solvent.

55 [0060] The first example of the solid polymeric electrolyte is essentially obtained by solidifying Composition (A) (precursor) composed of the urethaneacrylate, the organic polar solvent and the supporting electrolyte. If necessary, Composition (A) may be added with any suitable components as long as they are not obstructive to the achievement of the purpose of the Invention. Such components may be crosslinkers and photo- and thermal-polymerization initiators (light or heat).

60 [0061] Composition (A) is injected through the opening of one of the electrically conductive substrates disposed, facing each other to form a cell and then is cured in a conventional manner such that the first example of the solid polymeric electrolyte is sandwiched between the electrically conductive substrates. The term "curing" used herein designates a state where the component is cured with the progress of polymerization (polycondensation) or crosslinking and thus the composition does not flow at room temperature. The urethaneacrylate has the basic structure in the form of network by curing.

65 [0062] A second example of the polymeric solid electrolyte is obtained by solidifying a composition (hereinafter referred to as Composition (B)) which is used as a precursor and comprising an organic polar solvent, a supporting electrolyte, a monofunctional acryloyl-modified polyalkylene oxide and/or a polyfunctional acryloyl-modified polyalkylene oxide.

70 [0063] The mono-functional acryloyl-modified polyalkylene oxide is represented by the formula



wherein R^{22} , R^{23} , R^{24} and R^{25} may be the same or different and are each hydrogen and an alkyl group having 1-5 carbon atoms and n is an integer of greater than 1.

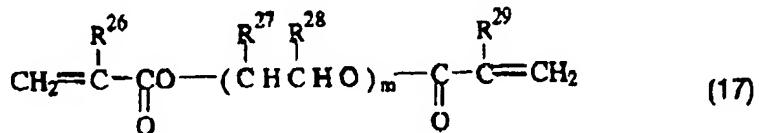
10 [0064] Specific examples of such alkyl group include methyl, ethyl, i-propyl, n-propyl, n-butyl, t-butyl and n-pentyl. Preferred for R^{22} , R^{23} and R^{24} are hydrogen and a methyl group. Preferred for R^{25} are hydrogen, a methyl and ethyl group.

[0065] n in formula (16) is an integer greater than 1, usually between 1 and 100, preferably 2 and 50, more preferably 2 and 30.

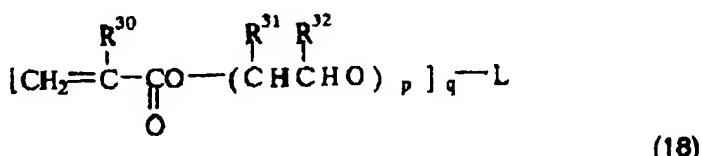
15 [0066] Specific examples of compounds represented by formula (16) are those having 1-100, preferably 2-50, more preferably 1-20 oxyalkylene units, such as methoxypolyethylene glycol methacrylate, methoxypolypropylene glycol methacrylate, ethoxypolyethylene glycol methacrylate, ethoxypolypropylene glycol methacrylate, methoxypolyethylene glycol acrylate, methoxypolypropylene glycol acrylate, ethoxypolyethylene glycol acrylate, ethoxypolypropylene glycol acrylate and mixtures thereof.

20 [0067] If n is greater than 2, the compound may be those having different oxyalkylene units, that is, copolymerized oxyalkylene units which for instance have 1-50, preferably 1-20 oxyethylene units and 1-50, preferably 1-20 oxypropylene units. Specific examples of such compounds are (ethylene · propylene) glycol methacrylate, ethoxypoly (ethylene · propylene) glycol methacrylate, methoxypoly (ethylene · propylene) glycol acrylate, ethoxypoly methoxypoly (ethylene · propylene) glycol acrylate and mixtures thereof.

25 [0068] Eligible polyfunctional acryloyl-modified polyalkylene oxide for Composition (B) is a bifunctional acryloyl-modified polyalkylene oxide or a polyfunctional acryloyl-modified polyalkylene oxide having more than three functional groups. The bifunctional acryloyl-modified polyalkylene oxide is represented by the formula



35 wherein R^{26} , R^{27} , R^{28} and R^{29} are each hydrogen and a $\text{C}_1\text{-}\text{C}_5$ alkyl group and m is an integer greater than 1. The polyfunctional acryloyl-modified polyalkylene oxide having more than three functional groups is represented by the formula



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wherein R^{30} , R^{31} and R^{32} are each hydrogen and a $\text{C}_1\text{-}\text{C}_5$ alkyl group, p is an integer greater than 1, q is an integer of 2-4 and L is a connecting group of valence indicated by q .

50 [0069] If R^{26} , R^{27} , R^{28} and R^{29} are alkyl groups, such alkyl groups may be methyl, ethyl, i-propyl, n-propyl, n-butyl, t-butyl, t-butyl and n-pentyl. Preferred for R^{26} , R^{27} , R^{28} and R^{29} are hydrogen and a methyl group.

[0070] m in formula (17) is an integer greater than 1, usually 1-100, preferably 2-50, more preferably 2-30. Preferred examples of compounds of formula (17) are those having 1-100, preferably 2-50, more preferably 1-20 oxyalkylene units such as polyethylene glycol diacrylate, polypropylene glycol dimethacrylate, polyethylene glycol diacrylate, polypropylene glycol dimethacrylate and mixtures thereof.

[0071] If m is greater than 2, the compounds of formula (17) may be those having different oxyalkylene units, that is, polymerized oxyalkylene unit having 1-50, preferably 1-20 oxyethylene units and 1-50, preferably 1-20 oxypropylene units, such as poly(ethylene · propylene) glycol dimethacrylate, poly(ethylene · propylene) glycol diacrylate and mixtures

thereof.

[0072] If R³⁰, R³¹ and R³² are alkyl groups, preferred are methyl, ethyl, i-propyl, n-propyl, n-butyl, t-butyl and n-pentyl groups. Particularly preferred for R³⁰, R³¹ and R³² are hydrogen and a methyl group.

[0073] p in formula (18) is an integer of usually between 1 and 100, preferably 2 and 50, more preferably 2 and 30.

5 [0074] q in formula (18) is a number of connecting group "L" and an integer between 2 and 4.

[0075] Connecting group "L" is a divalent, trivalent or quatravalent hydrocarbon group having 1-30, preferably 1-20 carbon atoms.

10 [0076] Such divalent hydrocarbon groups may be alkylene, arylene, arylalkylene, alkylarylene and hydrocarbon groups having those groups as the base skeleton. Specific examples of such hydrocarbon groups are those represented by the following formulae:

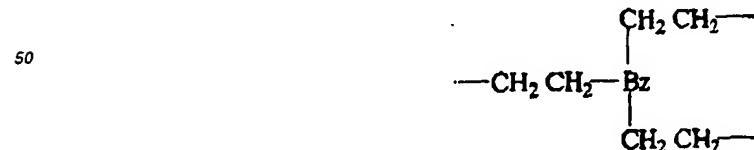


15 —CH₂ CH₂—



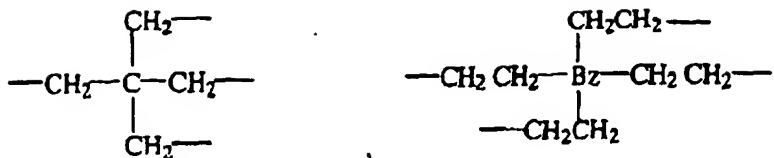
25 (Bz represents a benzene ring).

[0077] Such trivalent hydrocarbon groups may be alkyltryl, aryltryl, arylalkyltryl, alkylaryltryl and hydrocarbon groups having those groups as the base skeleton. Specific examples of such hydrocarbon groups are those represented by the following formulae:



55 [0078] The quatravalent hydrocarbon group may be alkyltetraryl, aryltetraryl, arylalkyltetraryl, alkylaryltetraryl or hydrocarbon groups having those groups as the base skeleton. Specific examples are those represented by the following formulae

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[0079] Specific examples of compounds of formula (18) are those having 1-100, preferably 2-50, more preferably 10-20 of an oxyalkylene units such as trimethylolpropanetri(polyethylene glycol acrylate), trimethylolpropanetri (polyethylene glycol methacrylate), trimethylolpropanetri (polypropylene glycol acrylate), trimethylolpropanetri (polypropylene glycol methacrylate), tetramethylolmethanetetra(polyethylene glycol acrylate), tetramethylolmethanetetra (polyethylene glycol methacrylate), tetramethylolmethanetetra(polypropylene glycol acrylate), tetramethylolmethanetetra(polypropylene glycol methacrylate), 2,2-bis[4-(acryloxypropoxy) phenyl]propane, 2,2-bis[4-(methacryloxypropoxy) phenyl]propane, 2,2-bis[4-(methacryloxypropoxy) phenyl]propane and mixtures thereof.

[0080] If p is more than 2, compounds of formula (18) may be those having different oxyalkylene units, that is, polymerized oxyalkylene units having 1-50, preferably 1-20 of oxyethylene units and 1-50, preferably 1-20 oxypropylene units. Specific examples of such Compounds include trimethylolpropanetri(poly(ethylene-propylene)glycol acrylate), trimethylolpropanetri(poly(ethylene-propylene)glycol methacrylate), tetramethylolmethanetetra(poly(ethylene-propylene)glycol acrylate), tetramethylolmethanetetra(poly(ethylene-propylene)glycol methacrylate) and mixtures thereof.

[0081] Needless to mention, there may be used the difunctional acryloyl-modified polyalkyleneoxide of formula (17) and the polyfunctional acryloyl-modified polyalkyleneoxide of formula (18) in combination. When these compounds are used in combination, the weight ratio of the compound of formula (17) to that of formula (18) is in the range between 0.01/99.9 and 99.9/0.01, preferably 1/99 and 99/1, more preferably 20/80 and 80/20. When the compound of formula (16) is used in combination with the compound of formula (17) or (18), the weight ratio therebetween is in the range of usually between 1/0.001 and 1/1, preferably 1/0.05 and 1/0.5.

[0082] The organic polar solvent and supporting electrolyte described with respect to Composition (A) are also eligible for Composition (B). The organic polar solvent should be added in an amount of 50-800, preferably 100-500 weight percent based on the total weight of the monofunctional acryloyl-modified polyalkyleneoxide and the polyfunctional acryloyl-modified polyalkyleneoxide.

[0083] The supporting electrolyte should be added in an amount of 1-30, preferably 3-20 weight percent based on the total weight of the monofunctional acryloyl-modified polyalkyleneoxide and the polyfunctional acryloyl-modified polyalkyleneoxide.

[0084] If necessary, Composition (B) may be added with another components optionally as long as they do not bother the achievement of the purpose of the invention. Such components may be photopolymerization initiators or thermal polymerization initiators. These initiators should be added in an amount of 0.05-5, preferably 0.01-3 weight percent based on the total weight of the monofunctional acryloyl-modified polyalkyleneoxide and the polyfunctional acryloyl-modified polyalkyleneoxide.

[0085] Composition (B) is injected through the opening of one of the electrically conductive substrates disposed, facing each other to form a cell and then is cured in a conventional manner so that the second example of the solid polymeric electrolyte is sandwiched between the electrically conductive substrates. The term "curing" used herein designates a state where the monofunctional acryloyl-modified polyalkyleneoxide or the polyfunctional acryloyl-modified polyalkyleneoxide is cured with the progress of polymerization (polycondensation) or crosslinking and thus the composition does not flow at room temperature. In this case, the monofunctional acryloyl-modified polyalkyleneoxide or the polyfunctional acryloyl-modified polyalkyleneoxide has the basic structure in the form of network.

[0086] According to the invention, any of the above-described liquid, gelatinized and solid electrolytes is generally injected into the cell. However, needless to mention, an electrolyte other than the above-described electrolytes may be injected into the cell. The gelatinized- and solid electrolytes are injected into the cell in the form of a precursor. As already described, the electrolyte or the precursor may be added with the electrochromic material beforehand. Upon the injection, there is selected a suitable method which can fill evenly the space between the two electrically conductive substrates with the electrolyte or the precursor. There is usually employed a vacuum injection method in which the hollow interior of the cell is evacuated so as to be ideally in vacuum and then the injection port opening of the cell is submerged into the liquid electrolyte or the precursor under atmospheric pressure such that the liquid electrolyte is supplied into the cell by utilizing the difference in pressure between the outside and inside of the cell.

[0087] Upon completion of the injection, before the precursor is gelatinized or solidified, the injection port opening of the cell is temporarily closed or sealed with a material which can be deformably inserted into the injection port. Eligible materials for this temporarily sealing are those which are resilient and resistant against the electrolyte or the

precursor thereof. Typical examples of such materials are a natural rubber and a synthetic rubber such as isoprene rubber, butadiene rubber, styrene-butadiene rubber, butyl rubber, ethylene-propylene rubber, chloroprene rubber, chlorosulfonated polyethylene, nitrile rubber, urethane rubber, polysulfide rubber, acrylic rubber, epichlorohydrin rubber, silicone rubber, fluorine rubber, hydrogenated nitrile rubber and the like.

5 [0088] After the temporarily sealing, the electrolyte or the precursor thereof adhered around the injection port is then removed by washing and thereafter the temporarily sealed injection port is secondarily sealed with an adhesive. Such an adhesive for sealing secondarily the injection port may be selected from various types of adhesives such as those of photo-, thermal-, room temperature-and electro beam- setting types. As a matter of course, there may be used acrylic, epoxy- and silicone-resin adhesives as well as other types of adhesives such as phenolic resin, urea resin, 10 epoxy resin, polyvinyl acetate, polyvinyl acetal, polyvinyl alcohol, acrylic and methacrylic esters, cyanoacrylate and polyamide. These may be used singular or in combination. Alternatively, these may be modified or added with fillers: [0089] In view of solvent resistance, the epoxy resin is found to be particularly superior. An acrylic-modified epoxy resin of photo-setting type is preferred. Preferred for such an acrylic-modified epoxy resin are those having 0.01-0.3 mol, preferably 0.05-0.2 mol of acrylic residue per mol of epoxy residue.

15 [0090] Thermo setting of the adhesive for bonding the sealing member to the cell may be conducted by using various types of heat source such as ovens, infrared heaters, electric heaters and surface type heat generators at a temperature ranging from room temperature to 150 °C, preferably room temperature to 100 °C. The time required for the thermo-setting is not restricted but is usually within 24 hours, preferably within one hour.

20 [0091] The photo-setting may be conducted by using various types of light sources such as low-, high- and ultrahigh-voltage mercury vapor lamps, a xenon lamp, an incandescent lamp and laser beams. The photo-setting of the adhesive may be conducted by exposing evenly the entire surfaces of the device to light after being applied with the adhesive. Alternatively, a step by step manner may be employed which is effected by scanning a gathered spot light over the device, for example, by moving a lamp or a light source or using a photoconductive material such as an optical fiber or a mirror. Practically preferred are methods using a 100W-1KW ultrahigh voltage mercury vapor lamp or a xenon-25 mercury vapor lamp. Among those methods, preferred are methods which guide the light from a light source of a 200W-500 W xenon-mercury vapor lamp using an optical fiber.

30 [0092] The secondary sealing of the present invention includes a method in which a sheet-like member is applied to the injecting port with an adhesive thereby increasing the durability of the sealing portion of the injection port. Eligible for this sheet-like member are any type of materials which can be bonded with an adhesive. Such materials are a glass sheet, a ceramic sheet and a synthetic resin sheet such as polyester, polyethylene terephthalate, polyamide, polysulfone, polyether sulfone, Polyether etherketone, polyphenylene sulfide, polycarbonate, polyimide, polymethyl methacrylate, polystyrene, tricellulose acetate, polymethylpentene, polysiloxane, polyethylene, polypropylene, polycellulose acetate, phenolic resin, urea resin, epoxy resin, polyvinyl acetate, polyvinyl acetal, polyvinyl alcohol, acrylic and methacrylic esters and cyanoacrylate.

35 [0093] According to the invention, since after the injection of the electrolyte or the precursor thereof the resilient sealing member closing the injection port of the cell can isolate the electrolyte or the precursor thereof injected thereinto from the influence of the outside of the cell, the complete removal of the electrolyte or the precursor thereof adhered around the injection port can be achieved merely by washing, resulting in that the adhesive for bonding the sealing member to the cell is free from the hindrance in adhesive capability caused by being mixed with the electrolyte or the precursor thereof. Furthermore, due to the injection port provided in the electrically conductive substrate, the inventive method, even upon the production of large size of electrochromic devices, is not only free from the risk that the sealing member comes out from the cell by the deformation thereof caused by stress and but also is contributive to enhance the durability of the sealing member because the sealing member is firmly fixed to the substrate by bonding with the adhesive.

40 [0094] The present invention will now be explained in further detail with reference to Examples, which are given only by way of illustration, but are not intended for limiting the invention.

Example 1

50 Preparation of Counterelectrode for Electrochromic Device

55 [0095] A pasty active carbon was prepared by mixing 80 g of active carbon powder manufactured by KURARE under the trade name of YR17, 40 g of graphite manufactured by NIPPON KOKUEN SHOJI CO., LTD. under the trade name of USSP, 343 g of a silicone resin manufactured by NIPPON UNICAR CO., LTD. under the trade name of RZ7703 and 25 g of butyl cellosolve. On an ITO glass substrate (a transparent electrically conductive glass produced by forming a layer having a thickness of 2,500 Å on a glass substrate by sputtering using an $In_2O_3:Sn$ target) of $10 \Omega/sq$ in electrical surface resistance, 2mm in thickness and 50cm x 50cm in size, the above-obtained active carbon paste was screen-printed to form a striped pattern; each stripe is 500 μm in width and 100 μm in height. The printed area was 20 % of

the total area of the electrode layer. The printed active carbon was cured by heating at a temperature of 180°C for 90 minutes thereby obtaining a counterelectrode.

Preparation of Electrochromic Electrode for Electrochromic Device

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[0096] On an ITO glass substrate which has an 4mm Ø opening located 15 mm apart from the sides of the substrate, of 10 Ω/sq in electrical surface resistance , 2mm in thickness and 50cm x 50cm in size, a 5000 Å thick tungsten oxide film was deposited at room temperature under the condition of 10-30 Å/second to obtain an electrochromic electrode.

10

[0097] The counterelectrode substrate and the electrochromic electrode substrate were placed in a 500 µm spaced apart opposing relationship, followed by sealing the peripheral edges of the opposed substrates thereby producing a hollow cell. A butyl rubber of 5mm wide had been applied to the peripheral edges as a primary sealant and a thermo-setting epoxy resin sealant of 5mm wide as a secondary sealant. The sealants were cured at 90°C for one hour.

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[0098] An electrolyte solution (1 mol/L concentration) containing a supporting electrolyte of LiClO₄ in γ -butyrolactone solvent was deaerated and then injected through the opening into the hollow cell in vacuum. Upon completion of the charging of the electrolyte, the opening was temporarily sealed by inserting thereinto a butyl rubber. After the removal of the electrolyte adhered on the cell surface around the butyl rubber by washing with an ethanol, the opening was coated with a photo-setting adhesive manufactured by THREE BOND under the trade name of 3025 and then applied to a light of 4,000 mJ by a high voltage mercury vapor lamp such that the adhesive is cured and the secondary sealing was completed, thereby obtaining an electrochromic device.

20

[0099] The coloring and bleaching test was carried out to measure the change of optical density. First, an electrical voltage of 1.5 V was applied across the electrochromic device for 150 seconds so as to be negative at the electrochromic electrode with respect to the counterelectrode. The electrochromic device was uniformly colored in blue, and the change in optical density at the center of the device was 0.50.

25

[0100] immediately after the 150-second coloration of the device, an electrical voltage of 1.0 V was in turn applied across the electrochromic electrode so as to be positive at the electrochromic electrode against the counterelectrode. The device was then bleached back to the colorless initial state.

[0101] The electrochromic device was left in an oven at 65 °C and a humidity of 95% for 1,000 hours. The device was taken out from the oven and the peel off at the sealing portion was not observed.

30

[0102] The electrochromic device was placed on 5 cm³ of acrylic supporting members situated under the corners of the device so as to be deformed by its weight for one month. The peel-off at the sealing portion was not observed.

Coloring and Bleaching Test

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[0103] 633nm of He-Ne laser beam expanded in diameter to 20mm by a beam expander was irradiated so as to pass through the center of the electrochromic device and the transmitted light was measured by using an Si photodiode. On applying an electrical voltage for coloration, the transmitted light intensity was measured every 5 seconds. If the transmitted light volume in t second after the coloration voltage is applied is expressed by T(t), the change in optical density is defined by the following equation:

40

$$\text{Change in Optical Density} = \log[T \text{ Bleach} / T(t)] \text{ (log is common logarithms)}$$

Example 2

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[0104] An electrochromic device was produced by following the procedures of Example 1 except that after a photo-setting adhesive manufactured by THREE BOND under the trade name of 3025 had been applied on the injection opening, a glass sheet of 3 cm x 3cm in size was place over the adhesive and then exposed to a light of 4,000 mJ by a high voltage mercury vapor lamp thereby completing the secondary sealing.

50

[0105] The coloring and bleaching test was carried out to measure the change of optical density. First, an electrical voltage of 1.5 V was applied across the electrochromic device for 150 seconds so as to be negative at the electrochromic electrode with respect to the counterelectrode. The electrochromic device was uniformly colored in blue, and the change in optical density at the center of the device was 0.50.

[0106] Immediately after the 150-second coloration of the device, an electrical voltage of 1.0 V was in turn applied across the electrochromic electrode so as to be positive at the electrochromic electrode against the counterelectrode.

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The device was then bleached back to the colorless initial state.

[0107] The electrochromic device was left in an oven at 65 °C and a humidity of 95% for 1,000 hours. The device was taken out from the oven and the peeling-off at the sealing portion was not observed.

[0108] The electrochromic device was placed on 5 cm³ of acrylic supporting members situated under the corners

of the device so as to be deformed by its weight for one month. The peel-off at the sealing portion was not observed.

Example 3

5 [0109] A photo-setting type electrolyte solution was prepared by admixing 20 weight percent of methoxytetraethylene glycol methacrylate and 0.02 weight percent of DAROCURE 1173 to an electrolyte solution (1 mol/L) containing an LiClO₄ electrolyte in a solvent of γ -butyrolactone.

10 [0110] The procedures of charging the electrolyte and sealing the opening (charging port) of Example 1 were followed except for using the above-obtained electrolyte. After completion of the secondary sealing of the opening with use of a photo-setting type adhesive, the electrolyte in the cell was cured by a light of 20 J in illumination from a high voltage mercury vapor lamp thereby providing an electrochromic device.

15 [0111] The coloring and bleaching test was carried out to measure the change of optical density. First, an electrical voltage of 1.5 V was applied across the electrochromic device for 150 seconds so as to be negative at the electrochromic electrode with respect to the counterelectrode. The electrochromic device was uniformly colored in blue, and the change in optical density at the center of the device was 0.48.

20 [0112] Immediately after the 150-second coloration of the device, an electrical voltage of 1.0 V was in turn applied across the electrochromic electrode so as to be positive at the electrochromic electrode against the counterelectrode. The device was then bleached back to the colorless initial state.

[0113] The electrochromic device was left in an oven at 65 °C and a humidity of 95% for 1,000 hours. The device was taken out from the oven and the peeling-off at the sealing portion was not observed.

Example 4

25 [0114] A cell was prepared by following the procedures of Example 1 except that the space between the substrates was changed to 200 μ m. An electrochromic device was prepared by charging the electrolyte of Example 1 in vacuum into the cell and following the rest of the procedures of Example 1.

30 [0115] The coloring and bleaching test was carried out to measure the change of optical density. First, an electrical voltage of 1.5 V was applied across the electrochromic device for 150 seconds so as to be negative at the electrochromic electrode with respect to the counterelectrode. The electrochromic device was uniformly colored in blue, and the change in optical density at the center of the device was 0.50.

[0116] Immediately after the 150-second coloration of the device, an electrical voltage of 1.0 V was in turn applied across the electrochromic electrode so as to be positive at the electrochromic electrode against the counterelectrode. The device was then bleached back to the colorless initial state.

35 [0117] The electrochromic device was left in an oven at 65 °C and a humidity of 95% for 1,000 hours. The device is taken out from the oven and the peeling-off at the sealing portion was not observed.

Comparative Example 1

40 [0118] A cell of the same in size as that produced in Example 1 was produced. Instead of making an opening in the surface of the substrate, this cell has an opening of 10 mm width made by omitting a part of sealing applied to the peripheral edge of the two opposing substrates.

[0119] An electrolyte solution (1 mol/L concentration) containing an electrolyte of LiClO₄ in γ -butyrolactone solvent was charged in vacuum into the above-obtained cell. After washing the charging port with an ethanol, it was coated with a photo-setting adhesive manufactured by THREE BOND under the trade name of 3025 and then exposed to a light of 4,000 mJ in illumination from a high voltage mercury vapor lamp thereby sealing the port.

45 [0120] The electrochromic device was left in an oven at 65 °C and a humidity of 95% for 400 hours. The device is taken out from the oven and the peeling-off was observed at the sealing portion of the port.

Comparative Example 2

50 [0121] An electrochromic device produced by following the procedures of Comparative Example 1 was placed on 50 cm³ of acrylic supporting members situated under the corners of the device so as to be deformed by its weight for one week. The peeling-off was observed at the portion of the sealing for the port.

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Claims

1. A method for producing an electrochromic device which comprises the steps of (a) assembling a hollow cell con-

stituting an electrochromic device by opposing two electrically conductive substrates, at least one of which is transparent and either of which is provided with an injection port for an electrolyte or the precursor, in a spaced-apart relationship with each other and sealing together the entire peripheral edges of the opposed substrates; (b) filling the inside of the hollow cell with an electrolyte or the precursor thereof by injecting through the injection port; (c) sealing temporarily the injection port with a material which can be deformably inserted into the port; and (d) sealing secondarily the temporarily sealed port by applying thereon only an adhesive or a sheet-like member over the adhesive.

- 5 2. A method for producing an electrochromic device according to claim 1 wherein said material is selected from the group consisting of a natural rubber, isoprene rubber, butadiene rubber, styrene-butadiene rubber, butyl rubber, ethylene-propylene rubber, chloroprene rubber, chlorosulfonated polyethylene, nitrile rubber, urethane rubber, polysulfide rubber, acrylic rubber, epichlorohydrin rubber, silicone rubber, fluorine rubber and hydrogenated nitrile.
- 10 3. A method for producing an electrochromic device according to claim 1 wherein said sheet-like member is selected from the group consisting of a glass sheet, a ceramic sheet and a synthetic resin sheet.
- 15 4. A method for producing an electrochromic device according to claim 3 wherein said synthetic resin sheet is formed from a material selected from the group consisting of polyethylene terephthalate, polyamide, polysulfone, polyether sulfone, polyether etherketone, polyphenylene sulfide, polycarbonate, polyimide, polymethyl methacrylate, poly-styrene, tricellulose acetate, polymethylpentene, polysiloxane, polyethylene, polypropylene, polycellulose acetate, phenolic resin, urea resin, epoxy resin, polyvinyl acetate, polyvinyl acetal, polyvinyl alcohol, acrylic and methacrylic esters and cyanoacrylate.

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